TRITERPENE COMPOUNDS FROM THE EPIGEAL MASS OF *Glycyrrhiza glabra*

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The epigeal part of *Glycyrrhiza glabra* is a valuable raw material [1, 2]. As reported previously [3], in the methanolysis products of the saponins isolated from this raw material we have detected two substances: with mp 238-240°C, IR spectrum: 3380, 1725 cm^{-1}, R_f 0.53 (Al_2O_3 activity grade II, $CHCl_3$); and with mp 265-267°C, IR spectrum: 3280, 1725 cm^{-1}, R_f 0.13 (in the same system). These substances form difficultly separable mixtures of methyl esters of triterpenoids not containing conjugated keto groups. Although such mixtures give a single spot on chromatograms in thin layers of Al_2O_3, the nonindividuality of each of them has been shown by their UV spectra (λ_{max} 280, 259, 250, 241 nm) which permit the assumption that the substances of each spot consist of mixtures of triterpenoids with homo- and heteroannular diene systems. To obtain individual compounds we used selenium dioxide, which can isomerize homoannular dienes into heteroannular dienes [4].

The substance with mp 265-267°C, R_f 0.13, was first acetylated in a mixture of acetic anhydride and pyridine (1:1). The diacetates of the methyl esters obtained (UV spectrum: λ_{max} 280, 259, 250 241 nm) with mp 210°C were heated with selenium dioxide in acetic acid for several hours. From the reaction products a methyl ester diacetate $C_{35}H_{52}O_6$ (M^+ 568) with mp 247°C was isolated. The UV spectrum of this substance had a triplet with λ_{max} 259, 250, 241 nm, which is characteristic for the UV spectrum of a heteroannular diene, was not observed. NMR spectrum: δ 2.05 (2 CH_3COO), 3.7 (OCH_3), 4.48 (quartet, 2 H, 1 CH_2OAc, J = 12 Hz), 4.65 (triplet, H at C_3); two quartets, 5.5 and 6.4 ppm, J = 10 Hz (olefinic protons).

For the methyl ester diacetate with mp 247°C that was isolated, the structure of the diacetate of 3,24-dihydroxyoleana-11,13(18)-dien-30-oate is extremely likely, since we obtained this substance from the diacetate of methyl 24-hydroxyglycyrrhetate (the structure of which has been shown previously [5]). The diacetate of methyl 24-hydroxyglycyrrhetate (mp 255°C) was converted on hydrogenation (PtO_2, acetic acid, 60 h) into the diacetate of methyl 24-hydroxydeoxoglycyrrhetate which, on being heated with selenium dioxide in glacial acetic acid, formed the diacetate of methyl 3,24-dihydroxyoleana-11,13(18)-dien-30-oate with mp 247°C (UV spectrum: λ_{max} 259, 250, 241 nm). In its properties, this substance was indistinguishable from that obtained from the mixture of natural compounds with mp 265°C; their IR and NMR spectra coincided, and mixtures of them gave no depression of the melting point.

Thus, the heteroannular diene present in the substance under investigation with mp 265-267°C is methyl 3,24-dihydroxyoleana-11,13(18)-dien-30-oate, and this is the first time that it has been found by the hydrolysis of licorice glycerides. The homoannular diene has not yet been identified, but it is apparently methyl 3,24-dihydroxyoleana-9(11)-12-dien-30-oate.

The substance with mp 238-240°C (R_f 0.53) was converted similarly (by acetylation and treatment with selenium dioxide) into the acetate of a methyl ester with mp 232-234°C (UV spectrum: λ_{max} 259, 250, 242 nm); the methyl ester corresponding to it, with mp 262-263°C, had properties agreeing with those of methyl 3β-hydroxyoleana-11,13(18)-dien-30-oate [6]. The homoannular diene present in the substance with mp 238-240°C was not isolated in the pure state.

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Mixtures of substances with a stable mp of 238-240°C, R_f 0.53, and with mp 265-267°C, R_f 0.13, were also found in minor amounts in the products of the acid hydrolysis of aqueous extracts of the roots of Korzhinskii's licorice and Urals licorice and in the roots of common licorice (*Gl. glabra*); they consisted of three heteroannular dienes and of probable homoannular dienes such as were found in the hydrolyzates of the herbage of *Gl. glabra*.

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